National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 918c

Potassium Chloride General and Ion Activity Standard

(Dried at 110 °C)

This Standard Reference Material (SRM) is intended for use as an analytical standard of known purity. It is intended primarily for use in the calibration and standardization of procedures for potassium (K) and chloride (Cl^-) determinations employed in clinical analysis, including those using ion-selective electrodes, and for routine critical evaluation of the daily working standards used in these procedures. This lot of potassium chloride (KCl) was prepared to ensure a material of high purity and homogeneity and has been assayed after heating at 110 °C to 120 °C. A unit of SRM 918c consists of a single glass bottle containing 30 g of the material.

Certified Values: Table 1 lists the certified values for this SRM, expressed as mass fractions, w, of KCl, K, and Cl^-. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1]. A certified value is the present best estimate of the true value. The expanded uncertainty, U, is calculated as $U = ku_c$, where u_c is the combined standard uncertainty calculated according to the ISO/JCGM Guide and its Supplement 1 [2,3]. The value of u_c is intended to represent, at the level of one standard deviation, the combined effect of inherent sources of uncertainty of the assay techniques, material heterogeneity, and applicable corrections for interfering trace elements. The respective values of the coverage factor, k, for each measurand in Table 1 correspond to an approximately 95 % level of confidence for the effective degrees of freedom, ν_{eff}, stated for the given measurand.

Reference Values: Table 2 lists reference values for the mass fraction of bromine (Br) and for alkalinity, expressed as potassium hydroxide (KOH). A reference value is a best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with an associated uncertainty that may reflect only measurement precision and may not include all other sources of uncertainty [1].

Information Values: Table 4 lists information values for trace elements. Information values are non-certified values that may be of interest and use to the SRM user, but insufficient information is available to provide an uncertainty associated with the value [1]. The information values are given to provide additional characterization of the material only. These values should not be used to monitor or assess analytical performance. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 918c** is valid, within the measurement uncertainty specified, until **01 October 2035**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM lot over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of the technical measurements leading to the certification of SRM 918c was provided by K.W. Pratt of the NIST Chemical Sciences Division.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 03 February 2016

Steven J. Choquette, Acting Director
Office of Reference Materials

Analytical measurements leading to the certification of SRM 918c were made by K.W. Pratt, J.R. Sieber, T.W. Vetter, and J.F. Waters of the NIST Chemical Sciences Division.

Statistical analyses were performed by W.F. Guthrie of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Calculation of Certified Values: The certified value for w_{KCl} is obtained by combining the results of independent coulometric and gravimetric analyses using the DerSimonian-Laird procedure [4]. Prior to computing the certified value, the results from the coulometric and gravimetric analyses were corrected for the following impurities: aluminum oxide (Al_2O_3), calcium chloride ($CaCl_2$), potassium bromide (KBr), potassium fluoride (KF), potassium hydroxide (KOH), potassium sulfate (K_2SO_4), rubidium chloride (RbCl), silicon dioxide (SiO_2), and sodium chloride (NaCl). The certified value for w_K is obtained by combining the direct result of the gravimetric analyses, corrected for the Al_2O_3, $CaCl_2$, NaCl, RbCl, and SiO_2 impurities; and the indirect w_K, calculated from the coulometric w_{KCl} and the additional K from the KBr, KF, KOH, and K_2SO_4 impurities. The corrected values are combined using the DerSimonian-Laird procedure. The certified value for w_{Cl} is obtained by combining the direct result of the coulometric analyses, corrected for interfering Br^-; and the indirect w_{Cl}, calculated from the gravimetric w_{KCl} and the additional Cl^- from the $CaCl_2$, NaCl, and RbCl impurities. The corrected values are combined using the DerSimonian-Laird procedure [4]. The corrections were obtained from the trace element determinations and the appropriate gravimetric factors [5]. A portion of the K is present in SRM 918c as KBr, KF, KOH, and K_2SO_4; and a portion of the chloride is present as $CaCl_2$, NaCl, and RbCl. Hence, the sum of the certified values for w_K and w_{Cl} does not equal the certified value for w_{KCl}. The certified values for the mass fractions of K, Cl, and KCl are metrologically traceable to the SI units for mass, current, and time in the coulometric assay; to the SI unit for mass in the gravimetric assay; and to the derived SI unit kilogram per kilogram for mass fraction (expressed as a percent) for the corrections for trace elements.

Table 1. Certified Values for SRM 918c

Measurand	Mass Fraction (%)	u_c (%)	ν_{eff}	Coverage Factor (k)	Expanded Uncertainty (%)
w_{KCl}	99.945	0.011	121	1.980	0.021
w_K	52.421	0.0053	133	1.978	0.010
w_{Cl^-}	47.5317	0.0040	27	2.052	0.0082

Calculation of Reference Values: The reference value, the measurand, for bromine (Br) is the mass fraction of Br as determined by wavelength-dispersive X-ray fluorescence analysis (WDXRF). The Br reference value is metrologically traceable to the derived SI unit kilogram per kilogram for mass fraction (expressed as micrograms per gram). The reference value, the measurand, for alkalinity (expressed as a mass fraction of KOH) was determined by pH measurements in a carbon dioxide-free 1.0 mol/L solution of dried SRM 918c. The reference value for the mass fraction of KOH is metrologically traceable to the quantity pH, to the primary measurement of pH, and to the SI unit for mass. The expanded uncertainty is calculated using $k = 2$.

Table 2. Reference Values for SRM 918c

Element or Property	Mass Fraction (µg/g)	Expanded Uncertainty (µg/g)
Bromine (Br)	50	27
Alkalinity (as KOH)	1.16	0.35

Information Values: Table 3 lists information values for the mass fractions of trace elements in SRM 918c. No other elements were detected. The information values were obtained by glow discharge mass spectrometry performed by a commercial laboratory.

Table 3. Information Values for SRM 918c

Element	Mass Fraction (µg/g)
Aluminum (Al)	0.5
Calcium (Ca)	<0.5
Fluorine (F)	<1
Sodium (Na)	14
Rubidium (Rb)	8
Sulfur (S)	6
Silicon (Si)	0.2

Information Values for Ionic Activity: Table 4 lists information values, in aqueous solution and at stated molalities, b, and corresponding mass fractions, w_K and w_{Cl}, of the following quantities at 25 °C: the mean activity coefficient, $\gamma_{\pm,KCl}$, of KCl; ionic activity coefficients, γ_K of potassium ion (K^+) and γ_{Cl} of chloride ion (Cl^-); and ionic activities, a_K and a_{Cl}, of K^+ and Cl^-. Values of $\gamma_{\pm,KCl}$, γ_K, and γ_{Cl} are each on the molality basis.

Table 4. Activity Coefficients and Ionic Activities for SRM 918c
Solutions of Specified Molalities

Molality (mol/kg)	Mass Fraction (µg/g)		Mean Activity Coefficient	Single-Ion Activity Coefficients		Ionic Activities	
b	w_K	w_{Cl}	$\gamma_{\pm,KCl}$	γ_K	γ_{Cl}	a_K	a_{Cl}
0.001	39.095	35.449	0.965	0.965	0.965	0.000965	0.000965
0.01	390.69	354.25	0.901	0.901	0.901	0.00901	0.00901
0.1	3880.9	3518.9	0.768	0.771	0.766	0.0771	0.0766
0.2	7704.8	6986.1	0.717	0.721	0.712	0.144	0.143
0.3	11473	10403	0.687	0.693	0.680	0.208	0.204
0.5	18847	17089	0.649	0.659	0.639	0.330	0.320
1.0	36386	32992	0.604	0.623	0.586	0.623	0.586
1.5	52749	47829	0.583	0.611	0.556	0.916	0.835
2.0	68050	61703	0.573	0.610	0.538	1.219	1.076

Values of $\gamma_\pm$ in Table 4 were obtained using Equation 1 [6]:

$$\lg \gamma_\pm = \frac{-AI^{½}}{1+BI^{½}} + \beta I + CI^2 + DI^3 \qquad (1)$$

In Equation 1, lg = $\log_{10}$; I is the ionic strength (identical to b for KCl solutions); A and B are the Debye-Hückel constants [6]; and β, C, and D are conventional constants specific to KCl [6]. The numerical values of these constants at 25 °C are:

A = 0.510 8
B = 1.295
β = 0.000 07
C = 0.003 599
D = –0.000 195 4

These constants are valid at molalities of KCl from 0 mol/kg to 4.8 mol/kg (saturation). For b < 0.1 mol/kg, the terms in Equation 1 containing β, C, and D may be neglected in the calculation.

The value of lg $\gamma_{\pm}$ at temperatures from 15 °C to 45 °C and at any molality of KCl from 0 mol/kg to 0.1 mol/kg may be obtained by using Equation 1 and temperature-dependent values of A and B calculated from Equations 2a and 2b, where t is the temperature in Celsius (°C):

$$A = 0.5108 + 8.4705\times10^{-4}(t-25) + 3.5498\times10^{-6}(t-25)^2 \quad (2a)$$

$$B = 1.295\left[1 + 4.7218\times10^{-4}(t-25)\right] \quad (2b)$$

The values for pK and pCl may then be calculated from lg $\gamma_{\pm}$ using the procedure described in reference 7 and osmotic coefficients for water given in reference 8.

Reference Values for pK and pCl: Table 5 lists reference values and associated uncertainties [6] for pK and pCl, where p denotes –lg, pK = p$a_{K,}$ and pCl = pa_{Cl}. The coverage factors and expanded uncertainties in Table 5 apply both to pK and to pCl. The pK and pCl values in Table 5 are metrologically traceable to the theoretical model used for the calculations (see above) and to the certified mass fractions of K and Cl in SRM 918c.

Table 5. Values of pK and pCl, Coverage Factors, and Uncertainties for SRM 918c Solutions of Specified Molalities.

Molality, b (mol·kg^{-1})	pK	pCl	Coverage Factor, k	Expanded Uncertainty, U
0.001	3.016	3.016	2	0.010
0.01	2.045	2.045	2	0.010
0.1	1.113	1.116	2	0.010
0.2	0.841	0.846	2	0.010
0.3	0.682	0.690	2	0.010
0.5	0.482	0.495	2	0.010
1.0	0.206	0.232	2	0.010
1.5	0.038	0.078	2	0.010

Instructions for gravimetric preparation of the solutions in Tables 4 and 5 are presented below (see "Preparation of SRM 918c Solutions of Specified Molalities").

INSTRUCTIONS FOR STORAGE AND USE

Storage: This SRM should be stored in its original bottle under normal laboratory conditions.

Use: Before it is sampled, the unit should be thoroughly mixed by carefully inverting and rotating the tightly sealed bottle. A minimum test portion mass of 200 mg should be used for analytical determinations. The bottle must be tightly re-capped after use and protected from moisture.

Drying Instructions: Dry the material for 4 h at 110 °C to 120 °C. After the SRM has been dried, store it in a desiccator over anhydrous magnesium perchlorate.

Preparation of SRM 918c Solutions of Specified Molalities: The gravimetric procedures in this section yield solutions with the molalities specified in Tables 4 and 5. The relative standard uncertainties specified for the weighings are selected such that the corresponding uncertainty in pK or pCl is negligible compared with the inherent uncertainty of the model used to calculate pK or pCl. The gravimetric factors are presented to six significant figures, to permit more accurate preparations where required for other applications. The target gravimetric factors given in Table 6 for SRM 918c yield molalities of K and Cl, b_K and b_{Cl}, that differ from the nominal value by less than six parts per million, relative.

Prepare these solutions following the instructions below and using the values in Table 6.

Quantities denoted by m' and associated gravimetric factors in this section include the effect of air buoyancy, i.e., they correspond to the balance indication in units of mass obtained in the laboratory (the "balance reading"), and they incorporate the certified values of w_K and w_{Cl} in SRM 918c.

Table 6. Dilution Information for Preparation of Solutions of SRM 918c of Specified Molalities

Molality, b (mol/kg)	Nominal Mass[(a)], m'_{918c} (g)	Gravimetric Factor (m'_{H_2O}/m'_{918c})
0.001	use serial dilution	---
0.01	0.30[(b)]	1339.96
0.1	1.5	133.996
0.2	3.0	66.9976
0.3	4.5	44.6649
0.5	7.5	26.7988
1.0	14.9	13.3992
1.5	22.4	8.93264
2.0	29.9	6.69938

[(a)] Unless otherwise noted, nominal mass of solution is 200 g.
[(b)] Nominal mass of solution is 400 g.

Locate the molality of the desired solution in the first column of Table 6, the corresponding nominal mass of SRM 918c in the second column, and the corresponding gravimetric factor (GF) in the third column. Weigh by difference the nominal (± 10 %) mass of dried (see above) SRM 918c, to a relative standard uncertainty of 0.1 %, into a clean, dry polyethylene bottle. For those solutions in Table 6 with $b_{KCl} > 0.01$ mol/kg, use a 250 mL bottle. For the solution with $b_{KCl} = 0.01$ mol/kg, use a 500 mL bottle. Multiply the exact delivered mass of SRM 918c, m'_{918c}, by the corresponding gravimetric factor given in the third column to obtain the exact mass of water, m'_{H_2O}, to add to the bottle. Add this mass of deionized water, weighed to a relative standard uncertainty of 0.1 %, to the bottle. The most convenient method is to tare the bottle containing the added SRM 918c on the balance, add the bulk of the water from a beaker and the last few grams using an adjustable pipet or dropper with a narrow tip. Cap the bottle and shake until the SRM 918c has totally dissolved. Gravimetric preparation in this manner eliminates the need to weigh exactly predetermined masses of solid samples. Proportionately smaller quantities of SRM 918c and water may be used in the preparations, provided that $m'_{918c} \geq 200$ mg.

The solution with a molality of 0.001 mol/kg is prepared by serial dilution of the 0.01 mol/kg or 0.1 mol/kg solution. To prepare it from the 0.01 mol/kg solution, add 20 g (nominal value, weighed to a relative standard uncertainty of 0.1 %) of the 0.01 mol/kg solution to a clean, dry 250 mL polyethylene bottle. Multiply the exact mass of the 0.01 mol/kg solution by the gravimetric factor 8.9933. Add this mass of water to the same bottle and mix. To prepare the 0.001 mol/kg solution from the 0.1 mol/kg solution, the corresponding approximate mass and gravimetric factor are 2.0 g (weighed to an accuracy of 0.1 mg) and 98.267, respectively. For either dilution, the mass of the concentrated solution may be varied within the limits set by the amount of available solution, bottle capacity, and resolution of the balances used.

SOURCE, HOMOGENEITY, AND ANALYSIS[(1)]

Source of Material: The KCl used for this SRM was obtained from a commercial supplier. The material was examined for compliance with the specification for reagent grade KCl as specified by the American Chemical Society [9]. The material was found to meet or exceed the minimum requirements in every respect.

Homogeneity: This SRM is homogeneous within the uncertainty limits for the nominal sample mass, 200 mg, used for the coulometric chloride assays. Samples less than 200 mg are not recommended in order to avoid possible heterogeneity with smaller sample sizes.

Assay Techniques: The coulometric assay value was obtained by automated titration [10] with coulometrically generated Ag^+ using potentiometric detection of the endpoint. The gravimetric assay value was obtained by converting test portions of SRM 918c material to K_2SO_4 (procedure based on reference 11). Corrections for air buoyancy were made using a density of 1.984 g/cm^3 for SRM 918c. Corrections for interfering trace contaminants in each determination were applied as described above.

[(1)] Certain commercial equipment, instruments, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

NOTICE TO USERS

This SRM is for research use only.

NIST encourages the use of its SRMs to establish metrological traceability for the user's measurement results, and NIST strives to maintain the SRM inventory supply. However, NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of SRMs as primary benchmarks for the quality and accuracy of the user's in-house (working) standards. As such, SRMs should be used to validate or otherwise assign values to the more routinely used standards in a laboratory. When the metrologically traceable values of such standards are assigned using this SRM for calibration, the uncertainties assigned to those values must include the uncertainty of the certified value of this SRM, appropriately combined with the uncertainties of the calibration measurements for the in-house standard. Comparisons between NIST SRMs and such working measurement standards should take place at intervals appropriate to the conservation of the SRM primary standard and the stability of relevant in-house standards. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

Possible Interfering Species: It is the responsibility of the user to evaluate which species may interfere with the application of this SRM and to apply any necessary corrections that affect the given application. The values in Tables 2 and 3 may be useful in this evaluation.

REFERENCES

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Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.